The State-Of-The-Art of the Coagulation/Flocculation Process

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THE STATE-OF-THE-ART OF THE COAGULATION/FLOCCULATION PROCESS

BY

DAVID W. BOUCK
B.S.E., Florida Technological University, 1971

RESEARCH REPORT

Submitted in partial fulfillment of the requirements for the degree of Master of Science in Environmental Systems Management in the Graduate Studies Program of Florida Technological University

Orlando, Florida
1973
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I hereby gratefully acknowledge the assistance provided by my advisor, Dr. Y. A. Yousef and the other committee members, Dr. W. M. McLeillon and Dr. Robert D. Doering, in the preparation of this graduate research report. I also wish to thank Mrs. Loretta Bartell for her kindness and perseverance in the format preparation and typing of the preliminary and final manuscripts.
This report has been prepared with the idea of briefly summarizing the most important principles underlying the coagulation/flocculation process as it applies to water and wastewater treatment. The production of potable water from a supply which has been contaminated by naturally-occurring or man-made pollutants has been an object of concern throughout history. Several broad aspects have been considered in the report, such as the history, the nature and physical chemistry of colloidal particles, the theories of and the factors affecting coagulation/flocculation, and control of the coagulation/flocculation process. It is advisable for those persons engaged in the dynamic environmental sciences to occasionally review the basic principles having to do with the processes being employed. In this light, this report provides a cursory review of pertinent literature with regard to the history, the stoichiometry and physical mechanisms involved, the techniques of process control and an assessment of the state-of-the-art of the coagulation/flocculation process. Of course, this discussion could have been written in more extensive detail, but the volume of such an enterprise would be excessive. For those desiring further information, an extensive bibliography of references has been appended.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section No.</th>
<th>Title</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Abstract</td>
<td>1</td>
</tr>
<tr>
<td>I.</td>
<td>DEFINITIONS</td>
<td>1</td>
</tr>
<tr>
<td>II.</td>
<td>INTRODUCTION</td>
<td>2</td>
</tr>
<tr>
<td>III.</td>
<td>HISTORY</td>
<td>3</td>
</tr>
<tr>
<td>IV.</td>
<td>MECHANISMS OF COAGULATION</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>1. Stability Forces</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>2. Instability Forces</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>3. Summary of Forces</td>
<td>20</td>
</tr>
<tr>
<td>V.</td>
<td>PHYSICAL FACTORS INFLUENCING COAGULATION/FLOCCULATION</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>1. Coagulation Kinetics</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>2. Flocculation Kinetics</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>3. Dosage and Process Control</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>4. Zeta Potential</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>5. Dosage and Behavior of Common Colloids</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>6. Summary of Physical Factors</td>
<td>28</td>
</tr>
<tr>
<td>VI.</td>
<td>COMMONLY USED COAGULANTS</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>1. Introduction</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>2. History</td>
<td>31</td>
</tr>
<tr>
<td>VII.</td>
<td>ASSESSMENT OF STATE-OF-THE-ART</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>1. Coagulation/Flocculation in Water Treatment</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>2. Coagulation/Flocculation in Wastewater Treatment</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>References</td>
<td>49</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure No.</th>
<th>Title</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Schematic Diagram of Typical Treatment Unit</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>Schematic Representation of Double-Layer Theory</td>
<td>14</td>
</tr>
<tr>
<td>3</td>
<td>Alum Coagulation of Typical Wastewater</td>
<td>43</td>
</tr>
<tr>
<td>4</td>
<td>Lime Coagulation of Typical Wastewater</td>
<td>45</td>
</tr>
</tbody>
</table>
DEFINITIONS

Historically, the terms "coagulation" and "flocculation" have been used indiscriminately to describe the process of removal of turbidity from water. There is, however, a clear distinction between the two terms.

The term coagulation is derived from the Latin "coagulare", meaning to drive together. This process describes the effect produced by the addition of a chemical to a colloidal dispersion, resulting in particle destabilization by a reduction of the forces tending to keep the particles apart.

The second stage of the formation of settleable particles from destabilized colloidal-sized particles is termed flocculation. This term also has its derivation from Latin, in this case "flocculare", meaning to form a floc. This was originally a description of a tuft of wood or a highly fibrous, porous structure. In contrast to coagulation, where the primary force is electrostatic or interionic, flocculation occurs by a chemical bridging or physical enmeshment mechanism. Flocculation is operationally obtained by gentle, extended mixing which transforms the submicroscopic coagulated particles into discrete, visible aggregates. At this stage, the particles are large and dense enough to settle rapidly under the influence of gravity and may be removed from suspension by sedimentation or filtration (29).
INTRODUCTION

With few exceptions, surface waters require some form of treatment before distribution as potable drinking supply. Natural waters, contaminated either by man or by nature, are likely to contain dissolved inorganic and organic substances, biological forms such as bacteria, algae and plankton, and suspended inorganic material. Coagulation, generally followed by filtration, is by far the most widely used process to remove the substances producing turbidity in water. These substances consist largely of clay minerals and microscopic organisms and occur in widely varying sizes, ranging from those large enough to settle rapidly, to those small enough to remain suspended for very long times.

The term "chemical treatment" has been popularly employed in reference to the process of "chemical coagulation". As a process for the treatment of water and wastewater, coagulation may be defined as the addition of chemicals, termed "coagulants", to effect destabilization and aggregation of dispersed materials, followed by the separation of the aggregated material from the suspending liquid.

The initial operation in the coagulation process is a rapid mix, frequently of less than a minute duration in which coagulants and chemicals for pH adjustment are distributed throughout the medium being treated. The mixing operation and chemical addition may consist of several stages. The next operation normally consists of flocculation, a slow mix lasting ten to forty minutes employed for the purpose of
promoting collisions between destabilized particles resulting in the formation of settleable aggregates. Figure 1 is a schematic representation of the treatment unit in which the coagulation/flocculation process takes place. The final operation in the process consists of separating the destabilized aggregates from the suspending liquid, usually by sedimentation or by flotation. Filtration may be substituted or used in conjunction with sedimentation for separation of aggregated materials.

Figure 1: Schematic Diagram of Typical Treatment Unit (12)

The principal application of the coagulation process is the transformation of non-settleable dispersed materials into aggregates, known as flocs, which are amenable to sedimentation or filtration. A discussion of the history of this process for water purification is presented.

HISTORY

Since the earliest days of man's existence, there has been a
relentless search for "pure" water. To get more or better water, ancient man either found other sources or, because of necessity, devised methods to improve the quality of the available water. Man's earliest standards of water quality were few (freedom from gross turbidity, taste and odor) compared to the standards accepted today. While our criteria of purity have become more complex and certainly more quantitative, the principles, methods, and materials for purifying water have remained remarkably similar, from the earliest recorded date of about 2000 B.C. down to the present.

Except for the developments of a last few decades, the history of water "treatment" is largely a record of empiricism and a description of an ancestral art rather than a scientific method. Through a continual evolvement of treatment techniques, man was not constrained to accept the quality of water that nature provided, but rather was able to modify it to meet his demands for increasingly higher standards of water quality.

Egyptian inscriptions of medical history offer the earliest recorded knowledge of water treatment, dating perhaps to 2000 B.C. In addition to heating and filtration, other methods of purification included the additions of a variety of mineral and vegetable substances. With time, other substances were found to be effective coagulants -- grain, nuts, potato starch and many others -- and were used to clarify turbid waters. In these cases, the coagulation preceded sedimentation
in a batch process, usually in jars or wooden storage vessels for private household consumption (25).

Alum, today's most widely used coagulant, also has an extensive history and was known to the early Egyptians. Its use, however, as a coagulant for potable water conditioning was first mentioned by Pliny (ca. 77 A.D.) who described both the use of lime (chalk of Rhodes) and alum (argilla of Italy) as useful for rendering bitter water potable. It is interesting to note that alum had become important in world trade, long before its use as a coagulant was practiced. By the 15th century, the preparation of purified alum required refining and manufacturing techniques. In 1461, Pope Pius II attempted to create a restrictive monopoly on the production of alum, and within years the enterprise required the manufacturing services of thousands of workers (29).

During the Dark Ages, the practice of water treatment, followed the decline of much of the known technology, but was revived during the 17th century by Sir Francis Bacon and others. By 1767, the common people of England were successfully treating muddy water in their households using alum in a batch process.

While coagulation as an aid to sedimentation and filtration of individual household and small industrial water supplies had been practiced from ancient times, its utilization in large industrial processes seems to have begun in the early part of the 19th century. The earliest
use of coagulation for the treatment of municipal water supplies was at Balton, England, in 1881. From 1885 onward, coagulation was widely used to precede another common unit process, filtration.

Coagulation for the improvement of public water supplies did not gain universal acceptance. Some notables in the 1800's protested against the coagulation and rapid filtration processes, and this continued during the late 19th and early 20th centuries.

In 1884 the first patent for a coagulation process was granted to Isaiah Smith Hyatt who, following the suggestion of Col. L. H. Gardner, then the superintendent of the New Orleans Water Company, described the use of perchloride of iron as a coagulant within his rapid-sand filtration treatment of turbid water. A year later, the Somerville and Puritan Water Company of New Jersey adopted Hyatt's coagulation-filtration system, and the use of coagulation was instilled as a full-scale method of treatment (29).

In 1885, Austin and Wilber of Rutgers University published the results of the first American investigation of alum as a coagulant. After testing a variety of metal salts, they concluded that none offered the advantages of alum. Subsequent scientific investigations in other sections of the country found alum the most suitable agent. Thus its use became more common and, by the turn of the century, coagulation (combined with rapid-sand filtration) was fully accepted in this country.
Excepting the use of iron perchloride by Hyatt in his first investigation of coagulation, aluminum sulfate dominated the field of coagulants in these early days. Nevertheless, iron, either as metal or as part of a salt, was widely employed as a coagulant of several water treatment plants in the late 19th century. William B. Bull in 1898 first introduced the use of a combination of ferrous sulfate and lime. In 1912, E. V. Ball reported the first use of chlorinated copperas (ferrous sulfate reacted with chlorine); however, this chemical was not tried again until 1928. It was then utilized by Hedgepeth and Olsen in the coagulation of highly colored water. This application served to focus attention on the iron salts, several of which are in use today. While such iron salts as ferric chloride, chlorinated copperas, and ferric sulfate are used, the sulfate of aluminum (alum) still is the most widely used coagulant.

Other metals capable of producing a hydrous oxide floc have been suggested as coagulant agents. Both sodium zincate and titanium salts have been studied, but have proved to possess no advantage over alum. Thus, they have been relegated as laboratory prototypes with no practical use in large scale water treatment (29).

Coagulation has progressed from the art of the early days' attempts to purify drinking water to today's sophisticated techniques, equipment and studies of many exotic coagulants for accomplishing the same objective on a much larger scale; but the alum of the ancient Chinese householder is still the foundation of today's efforts.
Recently in addition to studies of various chemical additives, analyses have been performed of the physical mechanisms of coagulation. The theories of colloidal chemistry pertaining to the coagulation/flocculation process will be discussed in an attempt to explain the stoichiometry involved.

MECHANISMS OF COAGULATION

Since the coagulation/flocculation process is concerned primarily with the separation of non-settleable suspended materials, the theory relating to the process deals with the behavior of finely divided particulate matter. In scientific language, non-settleable suspended materials are termed dispersions. Materials comprising dispersions in sewage and wastes may range in size from 0.1 μm to 100 μm. Since dispersed materials ranging in size from about 1 μm to 1 μ are termed colloids by chemists and physicists, it follows that non-settleable suspended solids present in wastewater exhibit the properties of colloids. This section will cover the present understanding of the mechanisms and stoichiometry of coagulation for removing colloidal impurities from water.

The colloids found in natural waters are principally clay particles and organic color; those in wastewaters include colloidal proteins and carbohydrates along with numerous other substances. All of them are commonly stabilized by negative charges at their surfaces.
Neutralization of the charge, which leads to destabilization and coagulation, is achieved by (1) interaction with ions of opposite charge, or (2) mutual coagulation with colloids of opposite charge (10).

Colloids may be classified in a number of ways. In the first place, they may be classified as sols or gels. Sols are, of course, colloids which have the appearance of true solutions, whereas gels have a jelly-like structure from which the name colloid (Greek: like glue) was derived.

Colloids may be classified as reversible and irreversible, and also as lyophobic and lyophillic. This classification has to do with the affinity of the colloidal particles for the dispersing medium. If the attraction between the colloidal particles and the dispersing medium is small, the colloid is termed lyophobic. If, on the other hand, the attraction between the colloidal particles and the dispersing medium is great, the colloid is termed lyophillic. The viscosity of the lyophobic colloids is usually about the same as that of the medium, and they are usually quite susceptible to coagulation. The viscosity of the lyophillic colloids, on the other hand, is usually much greater than that of the pure medium.

Finally the most important of all, colloids may be classified as positive or negative, since it may be readily shown that they bear electrical charges. There are a number of theories as to the source of this electrical charge, but these are beyond the scope of this
discussion. It is sufficient for us to know that the particles of some colloids bear a positive charge, whereas the particles of others bear a negative charge. It is also true that colloids may be prepared in essentially neutral condition and it is further necessary to note that colloids may change their electrical charges from positive to negative or the reverse as a result of a change in the external conditions. The latter point is very important in the theory of coagulation since it has been shown by numerous cases that both aluminum hydroxide and ferric hydroxide flocs may be either positive or negative. This has a most important bearing, not only on floc formation, but also on the completeness with which a coagulant will do the job it is supposed to perform (2).

At this point, it is necessary to consider the factors which cause colloidal particles to remain in suspension and subsequently those which result in coagulation. The "stability" of colloidal suspensions refers to the inherent property of colloids to remain dispersed, whereas "instability" describes the tendency of colloids to coalesce whenever particle contact occurs.

In the field of colloid science, at least two different approaches have been introduced to explain the basic mechanisms involved in the stability and instability of colloid systems. The first or older theory is the so-called chemical theory, which assumes that colloids are aggregates of definite chemical structural units and emphasizes specific chemical interactions between the coagulant and the colloids. According
to this theory, the coagulation of colloids is the result of a precipitation of insoluble complexes that are formed by specific chemical interactions. The second theory -- the physical or double-layer theory -- emphasizes the importance of the electrical double layers surrounding the colloidal particles in the solutions and the effects of counter-ion adsorption and zeta-potential reduction in the destabilization of colloidal systems. These two theories may appear to be contradictory, but they are not mutually exclusive.

1. Stability Forces

Since the objective of coagulation is to destabilize particles to form aggregates, it is important to consider the forces which cause stable suspensions. The most significant property of colloids is small size, which is responsible for initiating conditions favorable for creation and maintenance of dispersions. The most important stabilizing factors associated with colloidal dispersions are electrostatic repulsion and hydration. Both of these factors are surface phenomena which become important due to the large surface area offered by small particles. For instance, if a cubic centimeter possessing a surface area of 6 square centimeters were subdivided into colloidal-sized cubes of 10 m\(\mu\) on a side, the surface area would approach 6 million square centimeters. With surfaces of this magnitude, it is not surprising that factors relating to surface chemistry and surface physics are paramount in the behavior of colloidal systems (2).

When the surface of a colloid has a strong affinity for
water, it is classed as hydrophilic. Such particles tend to acquire a film of water molecules held by the surface. This phenomenon of hydration increases the stability of the dispersion, presumably by shielding the particle from the action of coagulants and from contact with other particles. Colloids with surfaces possessing a weak affinity for water are termed hydrophobic. Hydrophobic dispersions may be stabilized indirectly by hydration if a substance is present which has an affinity for both the surface of the particle and water. Such systems are described as protective colloids, and the intermediary substance is the protecting agent. The particles of such systems are considered to be coated with a film of the intermediate substance, which in turn attracts a film of water molecules; hence, the establishment of the electrical double layer theory.

The principal stabilizing factor for most hydrophobic colloidal systems is electrostatic force. The surface of colloidal particles has a tendency to acquire an electrical charge as a result of the ionization of surface components or the adsorption of ions from solution. In aqueous systems, hydrogen and hydroxyl ions are potential determining ions, even in the absence of other ionized solutes. Differences in properties of various ions will result in the preferential adsorption on the surfaces of colloids, with the result that all particles of similar composition acquire a charge of the same sign as the preferentially adsorbed ion. As a result of this charge development, a charge balance must be established in the vicinity of the colloid particle to fulfill the requirement of electroneutrality. The electrostatic
repulsion between charged particles stabilizes the dispersion by decreasing the probability of collisions which could effect aggregation of particles into flocs of considerable size (25).

Several theories have been advanced to quantitatively describe the concept of the electrical double layer. In its simplest form the theory states that hydrophobic particles suspended in water carry electrical charges at their surfaces. For colloids in natural waters, these charges are usually negative. The origin of these charges may be due to the dissociation of ionizable groups of the colloid itself or to the adsorption of low molecular weight ions onto its surface. As stated earlier, a charge balance must be established in the vicinity of the colloid particle to fulfill the requirement of electroneutrality.

An "electrical double-layer" theory of charge balance -- two surface charges separated by a constant distance -- has been described as a simple condenser in solution. The charges on the particle surface formed either the positive or negative portion, whereas the opposite charges (counter-ions) in the solution comprised the other portion. In the early 1900's, this oversimplified model was developed into a diffuse, double-layer model (Stern-Gouy model) in which part of the counter-ions remain in a compact layer on the charged colloid surface as a result of the strong electrostatic forces as well as Van der Waals forces. The other part of the counter-ions extends into the bulk of the solution and constitutes the diffuse layer. The effective thickness of this double-layer is influenced greatly by the overall ionic concentration.
of the solution, but relatively little by the size of the colloid.

Each colloidal particle can be described as a complicated entity consisting of several component layers. These are schematically illustrated in Figure 2.

![Figure 2: Schematic Representation of Double-Layer Theory (28)](image)

The particle surface is shown as a plane containing negatively charged ions. These ions are bound tightly to the surface of the particle and attract ions of opposite charge from the heterogeneous mixture of ions in the solution. This layer of cations (sometimes called counter-ions) is held near the particle by the electrostatic forces.

At increasing distances from the particle, the forces of attraction
quickly decrease, and there develops a diffuse layer of ions trailing out into the bulk solution. Caused by thermal agitation of the water molecules, this is depicted by the exponential decay shown in Figure 2.

At some distance from the particle and within the diffuse layer, there is a plane of shear representing the portion of the layer that will remain attached to the particle as it moves through the suspending solution. Hence, in a sense, the bound-water layer is considered an integral part of the charged-particle surface. It is important to note that the thickness of the double-layer relative to the particle diameter is extremely small. The distances shown in the figure have been exaggerated for illustrative purposes. For example, the thickness of the double-layer in a solution of monovalent ions at a concentration of $10^{-3}$ molar (about the concentration in surface water) is approximately 100 A or 0.01 μ (25).

The Stern-Gouy, electrical double-layer model gives a generally sound description of the distribution of the various potentials surrounding the charged particle. As a result of the electrical double-layer surrounding each particle, regions of electrical potential occur in a bulk solution that normally has a zero potential. The potential at the surface of the particle is called "total potential," which increases sharply with increasing proximity to the primary colloid surface. The second potential of interest is called the "zeta potential." It is located at the "plane of Shear"; that is, the boundary between the volume of the solvent adhering to the particle and the remainder of
the solution. This plane of shear essentially separates the water of hydration from free water (29).

The zeta potential is important because it is related to particle stability, and an approximate value of zeta potential can be easily calculated from electrophoretic measurements of particle mobility. It should be pointed out, however, that the zeta potential does not measure the total potential, but rather a portion of it. The stability of colloidal dispersions decreases as the zeta potential of component particles approaches a value of zero. Extensive application of zeta potential determinations has been suggested for the development and operational monitoring of an efficient coagulation process.

The net effect of the existence of electrical double-layers is to inhibit particle collision, and hence the double-layers increase stability to the suspension. Both the thickness of the double-layer and the density of the surface charge are dependent upon the concentration and valence of the ionic solution, and hence the stability of the suspended particles can be markedly affected by adding suitable ions to the solution.

2. Instability Forces

While electrical double-layer and surface hydration contribute to the stability of colloidal suspensions, there are factors which contribute to the destabilization of particles. These are principally gravitational forces, Van der Waals forces and Brownian movement. Due
to the small mass involved in colloidal systems, gravitational force is usually relatively small compared to other forces affecting the system. Van der Waals forces are attractive forces between particles that may be envisioned as molecular cohesive forces. As particles converge, such forces may increase in magnitude at a rate thousands of times that of electrostatic forces. Thus, although Van der Waals forces are negligible when masses are even slightly separated, they may become dominant if physical contact is induced. If the electrical forces of particle repulsion are diminished to permit particle collisions, the Van der Waals forces will cause the particles to cling together leading to the progressive agglomeration of particles into flocs (27).

Brownian movement is the random motion imparted to colloid particles as a result of impact with molecules of the suspending medium. Very minute particles suspended in water, particularly those with particle diameters $100\mu$ or less, are in constant motion. The energy of the particle motion is obtained from collisions with water molecules and is directly related to temperature, the energy increasing with increasing temperature. While this random motion will increase the probability of particle collisions, the contacts will not result in lasting unions unless the colloids have been previously destabilized. Moreover, for larger particles, Brownian movement is negligible. In order to promote destabilization, the creation of hydraulic gradients (such as caused by mixing or turbulence) is an effective way to promote particle collisions and aggregation.
The aggregation of dispersed particles is induced by the addition of chemical coagulants to decrease the effects of the stabilizing factors, hydration and zeta potential, and by agitation of the medium to encourage collisions between particles. Unfortunately, gross chemical dosages are normally required to materially affect the degree of hydration of colloids; therefore, hydrophilic dispersions may be difficult to treat economically by coagulation. Dispersions stabilized principally by electrostatic force are, in general, amenable to coagulation inasmuch as the addition of small doses of suitable electrolytes (coagulants) may cause a significant change in the zeta potential of the dispersion. Since most dispersions encountered in wastes are stabilized by negative charges, coagulants commonly contribute polyvalent cations, such as aluminum, ferric, ferrous and calcium. Organic poly-electrolytes are also effective coagulants or coagulant aids.

The reactions that occur following addition of polyvalent metal ions to wastewaters are not fully understood. Ferric or aluminum ions added to wastewater are rapidly distributed throughout the medium by a flash mix. These ions are active as evidenced by their ability to participate in the following reactions under favorable conditions:

a. The ions may react with constituents in solution such as hydroxides, carbonates, phosphates, sulfides and organic matter to form complex gelatinous precipitates of colloidal dimensions that are termed microflocs. Upon standing, the dominant composition of such precipitates is frequently a hydrous metal oxide. The microflocs may
possess a positive charge, or zeta potential, depending upon reaction conditions and factors such as composition of precipitate, pH and coagulant dosage. Low pH normally favors the acquisition of a positive charge. If a positive charge exists on the microflocs and the particles of the dispersion have a negative charge, aggregation of the microflocs and the dispersed particles of the waste will be induced by electrostatic attraction. If the microflocs possess a neutral or a slightly negative zeta potential, aggregation can still be induced through collisions. Some evidence suggests that aggregation of microflocs with dispersed waste constituents is the principal mechanism effecting coagulation in water treatment.

b. Highly charged ions may penetrate the film of ions and water surrounding the negatively charged particles of the dispersion which will partially neutralize the zeta potential, possibly to the point of inducing coagulation. This mechanism is probably of secondary importance in the coagulation of most wastes (24).

c. An increase in the concentration of cations in solution interferes with the transmission of electronegative forces of repulsion that stabilize dispersions with a negative charge. If the cations are polyvalent, the interference is more pronounced. Hence, the addition of polyvalent ions shrinks both the force field and the envelope boundary which serve to protect the particles from collisions. If ion exchange occurs between monovalent ions on the surface of the particles and polyvalent coagulant ions, destabilization of the dispersion is induced.
During the flocculation process involving gentle agitation, conditions are maintained to afford continued aggregation of the destabilized mixture of microflocs and waste constituents. The agitation is controlled so as to provide velocity gradients that will not disrupt the flocs of settleable size, yet will offer a high probability of collisions between suspended particles. In this stage of the process, continued purification may be envisioned through mechanical entrapment of suspended matter during floc aggregation and by continued adsorption of the great surface area provided by the floc (24).

3. Summary of Forces

A summary of the aforementioned forces which may be operating in any colloidal system is presented. The forces that tend to keep particles apart and hence lead to stable colloidal suspension are hydration, which results in a protective shield of water molecules, and electrical double-layer which produces electrical potentials that act as barriers to the close approach of other particles.

Instability of suspensions is the result of particle-to-particle contact, the essence of coagulation. The kinetic energy for particle dislocation is obtained from Brownian movement for the smaller particles. More importantly, it is obtained from external energy introduced into a colloidal suspension by mixing or turbulence which increases the particle collisions if the forces of repulsion or if the hydration layer are reduced. After particle contact is made, Van der Waals forces will cause the progressive agglomeration of colloidal
particles into flocs.

PHYSICAL FACTORS INFLUENCING COAGULATION/FLOCCULATION

In order to attain the optimum coagulation of a raw water, a very complex equilibrium consisting of many variables must be reached. Thus for a given water, there will be an interrelated optima of conditions such as pH, turbidity, chemical composition of the water, type of coagulant, as well as such physical factors as temperature and mixing conditions. Due to the complexity of the interrelations, it is necessary to empirically determine the proper dose and physical conditions for coagulation. A knowledge of the effects of the several variables on the coagulation process can lead to a more efficient application of empirical methods to full scale operation.

1. Coagulation Kinetics

The kinetics of coagulation due to the so-called physical-interaction mechanisms have not been fully understood. The simplest case of coagulation occurs when enough electrolyte has been added to reduce the double-layer barrier so that particle collisions resulting from Brownian movement produce irreversible coalescence. Studies have shown that under these conditions coagulation occurs rapidly.

Under conditions where only enough electrolyte has been added to partially reduce the thickness of the double-layer, coagulation occurs much more slowly. It has also been shown that the rate of
particle destabilization, and hence coagulation, is determined by particle size, shape and heterogeneity (29).

In addition, studies of the hydrolysis of metal salts have indicated that both hydroxide and hydrogen ions are involved -- thus pH plays an important role in coagulation kinetics. The pH of the water establishes the average charge of the hydrolysis products and consequently is significant in determining the rate of coagulation (29).

2. Flocculation Kinetics

The kinetics of colloid stabilization reactions can be divided into two rate processes, namely, the rate at which the coagulant is adsorbed from solution, and the rate at which the primary colloidal particles agglomerate forming larger aggregates. Studies have shown that cationic polyelectrolytes are readily adsorbed from solution onto the surfaces of negatively charged colloidal particles. Consequently, the rate-controlling step in this type of particle-destabilization reaction is the frequency of interparticle collisions.

The efficiency of polymer-destabilization reactions has been demonstrated to be greatly affected by the polymer concentration in the reacting system. Maximum turbidity-removal efficiency as determined by optical-density measurement of the settled suspensions, was shown to occur over a limited polymer dosage range, with dosages outside this range resulting in negligible turbidity reduction.
3. Dosage and Process Control

The quality of treated water and the costs of chemicals used in its production — dependent upon adequate control of the coagulation/flocculation processes — are of particular concern. Laboratory and in-plant control are essential to proper coagulation treatment for two basic reasons: first, plants which employ coagulation usually treat waters which are subject to wide variations in quality; and secondly, the best and most economical treatment of such waters cannot accurately be predicted, but must be established empirically by known testing and monitoring techniques. The coagulation and flocculation of water is influenced by a number of interrelated factors such as pH, color turbidity, mineral content and composition, temperature, the duration and degree of agitation during flocculation, and finally, the characteristics of the coagulant or flocculation aid in use (29).

The single, most widely used test to determine dosage and other parameters is the "jar test." The jar test is a batch process which attempts to simulate the full-scale coagulation/flocculation process, and it has been commonly and effectively used since its introduction in 1918. In its essentials, the jar test is a series of sample containers, the contents of which may be stirred by individual, mechanically operated stirrers. Samples to be treated are placed in the vessels and the treatment chemicals are added to the contents while stirring. The range of conditions, for example pH and coagulant dosages, are selected in an attempt to bracket the anticipated optimum conditions. After a short period of dispersion, the stirring is slowed to aid
floculation. The stirring is then stopped, and the flocs are allowed to settle. The supernatant is then analyzed for a variety of parameters such as color, turbidity, pH, and alkalinity.

The interpretation of the results of this test requires some determinative measure of the coagulation/floculation. A number of approaches have been used: (1) visual evaluation of floc size; (2) visual or photometric measurement of supernatant clarity or color; (3) time of appearance of first floc; (4) chemical determination of residual coagulant in supernatant; (5) rate of flocs settling; (6) measure of the electrophoretic mobility (zeta potential) of the particles; and (7) more recently, the filterability characteristics either through paper, membranes or miniaturized sand filters (29).

Moffet (18) suggests that the lack of an accepted jar test standard procedure makes it impossible for operators to compare results obtained, many times even in the same plant with the same raw water. He recommends the zeta potential method as a control of the coagulation process by monitoring the raw water for turbidity and zeta potential before chemical addition. He also suggests that monitoring of pH and zeta potential after the rapid chemical mix would assist in the control of the coagulation/floculation process.

4. Zeta Potential

Measurement of zeta potential is another procedure useful for the control of the coagulation process and for evaluating the
effectiveness of the treatment. Zeta potential of particles is never determined directly, but is calculated from a measurement of particle electrophoretic mobility. In the usual procedure, a special apparatus is used with which the behavior of suspended particles can be observed microscopically. Under the influence of an applied voltage, the charged particles will migrate to the poles of opposite polarity; the particle velocity can be visually measured by noting the time it takes the particles to travel a known distance. From these and other data, it is possible to calculate both the electrophoretic mobility and the zeta potential. The numerical value of the zeta potential that indicates optimum coagulation varies with the type of colloid to be removed from the water. Removal of organic colloids such as color, is generally obtained at zeta potentials near zero, whereas optimum clay turbidity removals are obtained when zeta potentials are slightly negative, ranging from -10 millivolts to perhaps -5 millivolts. But since a water is likely to contain a heterogeneous mixture of colloid types, the precise zeta potential which signals optimal coagulation must be established by other methods, such as the jar test or by correlation to actual plant performance.

The exact lack of correlation between zeta potential and coagulation has been explained on a theoretical basis. As indicated previously, the zeta potential is a measure of energy potential at the "plane of shear" between the particle complex and the bulk solution. However, the measurement of zeta potential is not an exact determination because the forces of attraction extend beyond the "plane of shear."
In practice, an empirical relationship can be established between zeta potential and coagulation with the optimum zeta potential usually negative with most water solutions.

Moffet states that monitoring zeta potential will result in plant control based on floc formed in the plant process, with no empirical relationships necessary; the method is fast and accurate; the determination indicates to the operator when to raise, lower or maintain the chemical dose; and the method will continually result in high effluent quality (18).

5. Dosage and Behavior of Common Colloids

The following statements (10) summarize the practical aspects of the indicated properties of colloids and the indicated dosage and behavior of common coagulants:

a. Coagulation is a time/concentration phenomenon. Concentration increases the opportunity for contact and decreases the time required for floc formation.

b. Stirring increases the opportunity for contact and decreases the time for floc formation, while promoting floc growth.

c. Iron and manganese naturally present in water can be called into use as coagulants and to speed their own removal.

d. The pH range of relative insolubility is 5 to 7 for aluminum, above 4 for ferric iron, and above 9.5 for ferrous iron.

e. In general ferric coagulants are useful over a wide pH range of 4.0 to 11.0. Ferric sulfate has been successfully used for color removal at low pH values; at high pH values it may be used for iron and manganese
removal and in the water softening process. For the latter uses, the insolubility of ferric hydroxides at high pH values makes ferric sulfate and the iron coagulants in general preferable to alum (29).

f. Aeration of the water prior to lime addition will make additional oxygen available and reduce lime-consuming carbon dioxide. The use of large amounts of lime may render the process uneconomical, unless treatment includes softening. At high pH values, natural color colloids are stabilized, and calcium carbonate may be precipitated on sand and other surfaces with which the water comes in contact after purification and during distribution. This is commonly called boiler scale.

g. If ferrous sulfate is to be used as a source of coagulant at low pH values, the ferrous iron may first be oxidized to the ferric state by adding a solution of chlorine to dissolved ferrous sulfate.

h. The presence or addition of negative ions extends the useful range of pH in the acid region. In accordance with the Schulze-Hardy rule, bivalent $\text{SO}_4^{2-}$ ions are more effective than monovalent $\text{Na}^+$ ions.

i. In soft waters, negatively charged color colloids are coagulated most effectively at pH values of 4 or less. The trivalent ions of aluminum and iron are then the precipitating agents. Excess amounts of $\text{Al}^{+++}$ and $\text{Fe}^{+++}$ may have to be removed as hydrous oxides by subsequent addition of alkaline substances. In practice, a pH value as low as 4 is seldom attained.

j. Color removal is sometimes improved by pre-chlorination of alum-treated waters. This may be due to the oxidation of ferrous iron. Iron in organic combination in highly colored waters has also been effectively oxidized and precipitated by potassium permanganate at pH of 8.8 to 9.8.

k. Alum reactions with natural constituents of water are varied and influenced by many factors making prediction of a stoichiometric reaction impossible. The simplest hypothetical reaction is between $\text{Al}^{3+}$ and $\text{OH}^-$ ions from the natural alkalinity or ionization of water. Consumption of the hydroxide ions in the water will decrease the alkalinity, which if inadequate for the alum dosage, may be supplemented by the addition of hydrated lime, soda ash or caustic
soda. These chemicals maintain the optimum pH range for alum coagulation.

1. Sodium aluminate differs from alum in that its reaction is alkaline instead of acidic. It is generally used in conjunction with alum in the "double coagulation" of highly colored waters to raise the pH above the relative solubility range for aluminum (pH 5-7), causing soluble aluminum to flocculate as aluminum hydroxide.

m. Sodium aluminate is also often used in lime-soda softening of water to coagulate the fine precipitates of calcium carbonate and magnesium hydroxide from previous softening reactions.

n. The coagulation of very clear waters may be improved by the addition of finely divided clay, activated silica or other coagulant aids. These provide nuclei about which the precipitate can collect. They also weight the floc and hasten the sedimentation process (29).

6. Summary of Physical Factors

The removal of suspended material from raw water has ancient beginnings. It has only been within the last 50 years that water treatment consisting of coagulation, flocculation, and filtration has progressed from an ancestral art to a technology based on scientific principles. It is now generally recognized that coagulation and flocculation are a specialized branch of colloid chemistry, itself a branch of physical chemistry, that considers the behavior and properties of minute particles. The very small size and great numbers of particles in water make the surfaces of these particles much more important than the weight or density of the particles. Thus, interfacial or colloidal properties dominate in the coagulation and flocculation processes.

Surfaces of particles either contain or acquire electrical
charges that lead to forces that cause particles to be attracted or repulsed. In addition, forces inherent in atomic structure, such as Van der Waals forces, become involved. As a result of the presence of electrical charges and in order to maintain electrical neutrality, particles are surrounded with a shell of ions of opposite charge, generally described as the electrical double-layer. In the absence of external influences on the colloidal system, such suspensions are completely stable for very long times. Instability, leading to agglomeration of individual colloids, is readily produced by such external influences as chemical coagulants, polyelectrolytes and mixing.

The process of coagulation and flocculation is sensitive to many variables such as pH, coagulant used, dosage concentration, and kind of anions, to mention just a few. Of the many variables that can be controlled in a full scale operation, that of pH adjustment is of primary importance. But to obtain the most efficient removal of particles, other conditions in addition to the solution's pH must be determined, if not controlled.

Several mechanisms have been proposed for the removal of particles by metal coagulants and polymers, such as electrical double-layer compaction, neutralization of electrical charges, adsorption and bridging, and mechanical enmeshment. It seems likely that all of these processes may be involved in varying degrees in any coagulation/flocculation system.
An understanding of the mechanisms of the coagulation/flocculation process was significantly advanced by the recent knowledge of the behavior of metal coagulants in aqueous solutions. Unfortunately, a better understanding of the mechanisms involved in colloidal chemistry has not provided the means to predict the effectiveness of coagulation. Thus the practitioner has had to rely on empirical techniques to guide him in the treatment of water. The jar test, with its many variants, still remains the primary technique, although other more technical methods such as turbidity monitoring, filtration devices, and electrophoretic mobility are being more widely adopted (29).

Until recently, little advancement was made in providing the practical operator with other than the traditional and empirically-tested coagulants, based on aluminum and iron salts. The recent introduction of polymeric aids to coagulation and polyelectrolyte coagulants has greatly changed this. While the ideal polyelectrolyte has not yet been discovered, varying combinations of these compounds has been widely successful. It seems inevitable that these compounds will find greater and greater usefulness in the water industry in the future (24).

COMMONLY USED COAGULANTS

1. Introduction

Having now reviewed some of the principles of colloidal chemistry, we are in a position to examine the known facts of coagulation and to attempt to explain them in terms of the behavior of colloids.
We have learned that both color and turbidity present in natural water are present in the form of negative colloids. That leads us to the conclusion that for their coagulation we will need to employ either a positive ion or a positive colloid or both. As it happens, both agents take place in the phenomenon of floc formation. By examining the chemical formulas for commonly used coagulants, we see that they have positive ions whose most common valence is three. Though chemists have carefully searched the periodic table of the elements and have made efforts to employ other elements of the same valence and elements of higher valence, the most effective and widely used coagulant salts are alum, ferric sulfate and ferric chloride (10).

2. History

It is hardly worthwhile to attempt a complete history of the coagulants which have been used in water treatment since most are familiar and receive frequent mention in the literature. As has been previously stated aluminum sulfate (alum) continues to be the most widely used material of its kind, but there appears to be an increasing tendency toward the use of ferric chloride, where readily available. Sodium aluminate often finds application, especially in industrial water treatment and often in combination with alum. Ferric chloride and chlorinated copperas have been used and in the Midwest a combination of ferrous sulfate and lime has been widely used, mainly for the removal of turbidity. It was one of the first coagulants to be used in this country, having been used in Quincy, Illinois in 1898 (4).
The use of bentonite as a coagulant aid has been suggested, but although it proved successful in some cases, it has not been generally accepted. The use of activated silica as an accessory coagulant deserves special mention. A solution of sodium silicate, activated with sulfuric acid, aluminum sulfate, ammonium sulfate, chlorine, carbon dioxide and so forth, yields a stable solution bearing a high negative charge. In the acid range, it effectively promotes coagulation and floc formation with either alum or ferric sulfate. It is not generally recognized, however, that activated silica may act as a coagulant in the truest sense of the word since, in softening many raw waters by the lime-soda process, it results in the formation of a better-formed and better-settling sludge than either alum or ferric sulfate.

ASSESSMENT OF STATE OF THE ART

It is advisable for those who are engaged in any phase of water and wastewater treatment to occasionally review and assess the "state of the art" applications of the basic principles previously described. This section is going to attempt this in two parts -- one concerned with coagulation/flocculation in water treatment and the second in wastewater treatment.

1. Coagulation/Flocculation in Water Treatment

The past decade has witnessed a large increase in the production of softened water. There are two main reasons for this increase. In the first place, new industrial processes have created a demand for
large volumes of soft water. Secondly, there is an increased appreciation on the part of the domestic consumer of both the aesthetic advantages and economic savings resulting from the use of softened water. The result has been that several years ago water softening was practiced only in so-called "hard water" areas; it has now spread to all portions of this country and much of the world.

There are two main processes employed in the softening of water. The first is the lime or lime-soda process and the second is the zeolite process. The zeolite method of softening takes advantage of the remarkable property of certain naturally-occurring aluminosilicates for base exchange; that is, these materials have the property of reversibly exchanging bivalent materials such as calcium, magnesium and iron for monovalent elements and ions such as sodium, potassium and ammonium. In addition to the natural mineral glauconite, synthetic zeolites have been produced which have substantially greater exchange capacities than the natural products (29).

The lime-soda ash process uses chemical precipitation to remove dissolved substances from the raw water. The added chemicals are soluble, their ions reacting with the ions in the raw water to form precipitates which are then removed by sedimentation and filtration. The softening of water occurs by the addition of lime to precipitate the carbonate hardness and the addition of soda ash to remove the non-carbonate hardness.
In the lime or lime-soda ash softening process, precipitates of calcium and magnesium are produced which must be removed by sedimentation and filtration before distribution to the consumer. Difficulties in the sedimentation process have historically been deficiencies in the coagulation/flocculation process whereby the mechanisms for removal are hindered by some chemical or physical factors. These characteristically include: fine, slow-settling flocs during low temperature coagulation, slow-settling flocs in low mineralized waters with high color content, fragile flocs which are fragmented by hydraulic forces during sedimentation and filtration, and the interference of coagulation by substances in the raw water (29).

Even though studies have shown a great many materials to be aids to the clarification of treated waters, the particular choice is largely empirical and must be based on the characteristics of the water being treated. The most widely used materials may be roughly classified as: coagulants (aluminum and ferric salts) and coagulant or flocculation aids (oxidizing agents, absorbents and weighting agents, activated silica and polyelectrolytes).

a. Coagulants - Particularly in waters with low magnesium concentrations, the precipitates formed in the softening process are of such particle size as to approach the colloidal state, and consequently, settling occurs with difficulty, if at all. It is usual practice to employ a small amount of some suitable coagulant as an aid to sedimentation. For this purpose, the common aluminum and ferric salts are often
employed, generally in dosages of 10 mg/liter or less. However, since these salts increase the lime requirements and add residual noncarbonate hardness, it has been shown that the use of sodium aluminate can be beneficial. It functions both as a coagulant and a softening agent by virtue of the excess sodium hydroxide in the commercial product. Dosages are commonly around 5 mg/liter (29).

b. Oxidizing Agents - Often dissolved organic compounds contribute problems in clarification and color removal in treated water. The effects of these compounds can often be eliminated or minimized by the use of oxidizing agents such as chlorine, chlorine dioxide, ozone, potassium permanganate and "Oxinite" a commercial combination of various oxides of nitrogen. The most common application in water treatment is "breakpoint chlorination" in which sufficient chlorine is added to satisfy chlorine demand, oxidizing the organic compounds and providing disinfection as well. The exact dosage for a given water must be predetermined by appropriate testing.

c. Weighting Agents - Bentonitic clays have been used as coagulant aids in treating waters with high color, low turbidity and low mineral content. The addition of the clay, with its inherent high specific gravity, results in a "weighting action" on slow settling floc. Often, the floc produced from highly colored waters by iron or aluminum coagulants is too light and small to settle readily. The addition of 10-50 mg/liter of bentonite frequently can result in formation of rapidly settling floc, adsorbing color and other organic matter and
broadening the pH range required for optimum coagulation.

Other weighting agents besides clay have been used, such as powdered silica, limestone (which provides weighting capabilities and additional alkalinity) and activated carbon (which provides exceptional adsorptive capacity) (29).

d. Activated Silica - Until recent discoveries of the effects of polyelectrolytes as coagulant aids, activated silica was thought to be the only available chemical to greatly aid the coagulation/flocculation process. From its inception in the late 1930's, the addition of sodium silicate solution has had a pronounced effect on coagulation with alum. The use of activated silica has now become widespread, with dosages approximately 7 to 11 per cent of the alum dose required.

In the late 1940's, the widespread use of activated silica in a plant-scale operation of lime or lime-soda ash softening was accepted. Sodium silicate activated with ammonium sulfate was first used for this purpose in Fort Lauderdale, replacing 4 grains per gallon of alum coagulant and effecting very substantial cost savings (15). Although activated silica was originally suggested as a coagulant aid, the many instances where it has been used as the only coagulant make it possible to designate it a true coagulant.

Depending upon the conditions of its use, such as pH and order of application, activated silica can produce considerable process
benefits. It offers the advantages of: increased rate of coagulation, reduced coagulant dose, and extended pH range of optimum coagulation. It can also increase the rate of flocculation, produce larger and denser (hence faster-settling) flocs and toughen the floc so that filtration after sedimentation is improved. In this application, dosages of less than 1 mg/liter SiO₂ have produced floc enabling increased filter rates and longer run times, while acting as a filter aid to reduce the amount of floc passing through the filter (29).

e. Polyelectrolytes - Polyelectrolytes, both anionic and cationic, have shown promise as coagulant aids in softening. Although they are not as widely used as activated silica, the interaction of the polymer and electrolyte in water treatment is not new. Naturally-occurring biocolloids such as starch, starch derivatives, cellulose compounds, polysaccharide gums and proteinaceous materials are the basis from which the synthetic polymers were patterned. The extremely long molecular chain and the high charge density of the polyelectrolyte give an indication of its behavior as a coagulant aid. The advantage of the synthetic product over the naturally-occurring types is that the molecule can be tailored to meet specific requirements.

In practical terms, the use of a polyelectrolyte provides a means of increasing the size and settling rate of floc. The number of polymer molecules in solution, even at low dosages, exceeds by several orders of magnitude the number of colloids and suspended particles present in the water. Typically, hundreds of polymer molecules are available
for each particle of turbidity. The polyelectrolyte has no destabilization characteristics, but rather uses a "bridging" mechanism to assist in the agglomeration of suspended flocs and colloidal particles. The theory postulates that the long polymeric molecules attach themselves to suspended particles with part of the chain extending into the suspending medium. This free end is then free to adsorb onto another suspended particle, forming a bridge between the two flocs or suspended particles. The progressive linking of more and more particles results in floc whose eventual size is limited by its ability to withstand the hydraulic shear gradient imposed on it by agitation or turbulence.

Theoretical and experimental studies have been conducted to explain why an optimum range of polymer dose exists where too little leads to weak flocculation, and too much results in a dispersion. Optimum flocculation is said to occur whenever approximately 50 per cent of the surface of the suspended particle is covered with polymer segments. If too few adsorption sites are occupied by polymeric molecules, the possibility of interparticle bridging is reduced, and bonds may not be strong enough to withstand operational shearing forces resulting in resuspension of the particles. Conversely, if too many adsorption sites on the particle are occupied by polymer, bridging will be restricted, and if all sites are occupied, bridging will be impossible, both conditions leading to a dispersed rather than a flocculated system (29).

Since polyelectrolytes are synthetic constituents being used to treat municipal water supplies, the problem of toxicity has to be
addressed. Commonly the polyelectrolytes are manufactured from monomers that are, in some cases, relatively toxic. To provide assistance to the users and to the individual state and local health departments, the U.S. Public Health Service has established a procedure for reviewing and evaluating those products used in treating drinking water (29). Periodic lists of approved products and their concentrations are distributed by regulatory agencies, such as the Environmental Protection Agency, and are published in the professional journals from time to time.

Summarizing, precipitates of calcium and magnesium (formed in the water softening process) are often so fine as to approach colloidal sizes, in which case a coagulant or coagulant aid is required to induce coagulation and sedimentation. The common aluminum and iron salts are frequently used for this purpose, generally in dosages of 10 mg/liter or less. Since these salts often contribute to increased lime requirements in the softening process and add noncarbonate hardness, sodium aluminate has often been used. It functions both as a coagulant and a softening agent and dosages of approximately 5 mg/liter are commonly used. Activated silica has been widely used in softening as a coagulant. For this purpose, the activated silica is generally added prior to the lime, although other points of application have been recommended for certain waters. Dosages generally range from 2 to 5 mg/liter. Polyelectrolytes, exhibiting characteristics of both polymers and electrolytes in solution are becoming more widely used. Both anionic and cationic, these natural and synthetic compounds promote flocculation rather than coagulation and aid in the solids separation process.
2. Coagulation/Flocculation in Wastewater Treatment

The utilization of chemical coagulation/flocculation in wastewater treatment involves the addition of chemicals for the expressed purposes of improving plant performance and removing specific components contained in the wastewater. In the past, chemical precipitation was used to enhance the degree of suspended solids and BOD removal where there were seasonal variations in the concentration of the sewage (wastes from canneries, for example), where an intermediate degree of treatment was required, and as an aid to the sedimentation process. As recently as 1970, interest in chemical precipitation has been renewed because (1) it can be used effectively for the removal of phosphorus and (2) it can be combined with activated carbon adsorption to provide complete wastewater treatment, bypassing the need for biological treatment and, at the same time, providing more effective removal of the organics in wastewater that are resistant to biological treatment (28).

The need to provide more efficient removal of the organic compounds and plant nutrients (nitrogen and phosphorus) contained in various wastewaters is providing the impetus for the renewed interest in chemical aids to precipitation. Processes have been developed for the complete treatment of raw wastewater and for use in conjunction with conventional forms of biological treatment.

Facilities designed for the complete treatment of wastes are often physical-chemical processes. The unit process of lime precipitation is used for phosphorus removal. While the lime dosage required
is often calculated as a function of the raw wastewater alkalinity, the required dosage can only be determined by pilot plant testing on the actual wastes. Where removal of nitrogen compounds is not a requirement, the complete treatment process may be modified with alum used as the primary precipitant. After coagulation/flocculation and sedimentation, the effluent is passed through multi-media filters to remove any residual floc.

a. Phosphorus Removal - Phosphorus removal from wastewater has been carried out on a plant scale basis for several years and is no longer considered an experimental process. A measure of the progression of the state-of-the-art of phosphorus removal was indicated by the more than 100 references cited by Minton and Carlson (17) in their review of combined biological-chemical processes. The precise mechanism of phosphorus removal has long been a source of discord among many researchers. Mechanisms mentioned in extensive literature include precipitation, coagulation/flocculation, and adsorption. In most empirical applications, the combination of all three must occur in order to achieve a high degree of phosphorus removal. That is, the chemicals normally used (lime or alum) react with orthophosphate and form a fine, colloidal phosphate precipitate. At the same time, the chemical reacts to the natural alkalinity of the raw wastewater to form a large floc. This floc coagulates the fine colloidal phosphate precipitate and suspended solids, as well as adsorbing some of the organic bound phosphorus (9).

Chemicals that are used for phosphorus removal include
aluminum salts, ferric salts and lime. When alum $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$
is added to wastewater, the following reaction occurs:

$$\text{Al}_2(\text{SO}_4)_3 + 6\text{HCO}_3^- \rightarrow 2\text{Al(OH)}_3\downarrow + 3\text{SO}_4^{2-} + 6\text{CO}_2$$

Further, in the presence of phosphates, this reaction also proceeds:

$$\text{Al}_2(\text{SO}_4)_3 + 2\text{PO}_4^{3-} \rightarrow 2\text{AlPO}_4\downarrow + 3\text{SO}_4^{2-}$$

The two reactions compete for the aluminum ions provided by the addition of alum. The aluminum hydroxide floc enmeshes and adsorbs colloidal sewage or aluminum phosphate particles, assisting phosphorus removal by chemically clarifying the wastewater. Theoretically, the ratio of aluminum ion to phosphorus ion for phosphorus removal is 0.87 to 1. In plant practice, the ratio of aluminum to phosphorus is on the order of 2-3 to 1, depending upon the chemical characteristics of the raw wastewater and the required final phosphorus concentration. Figure 3 depicts the effect of alum dose on the final phosphorus concentration for hard and soft wastewaters.

The dominant reaction in iron coagulants is the combination of ferric and phosphate ions to precipitate as $\text{FePO}_4$. Experience has shown that efficient phosphate removal requires an excess of ferric ion to ensure the formation of ferric hydroxide as an auxiliary aid to removal. The stoichiometric dose (1.8 mg/l Fe per mg/l P) is supplemented by at least 10 mg/l of iron for hydroxide formation. Typically the iron requirements for municipal wastewaters range from 15-30 mg/l as Fe to reduce phosphorus on the order of 80 to 90 percent. The iron
hydroxide floc often requires a polymer as an aid to sedimentation because of difficulty in settling to produce a clear supernatant.

Plants are achieving various levels of phosphate removal by addition to the primary clarifier, to the aeration tank or in separate chemical clarifiers of secondary effluent. In these applications, final effluent concentrations of 1 to 3 mg/l as P are commonly obtained. To achieve final concentration less than this effluent filtration must be employed and carefully operated (9).

In cases where iron or aluminum salts are incorporated in biological treatment processes, care must be exercised to ensure that the rate of chemical solids formation does not exceed the rate of biological sludge formation. No problems, other than an increased organic load to the sludge digester, have been reported as long as the activated
sludge process is operated as a high growth rate biological system.

In the lime coagulation process, lime reacts with the bicarbonate alkalinity to form calcium carbonate and also reacts with phosphate to precipitate hydroxyapatite. While orthophosphate is precipitated by calcium ions forming hydroxyapatite, polyphosphate is removed by adsorption on other particles of hydroxyapatite, as well as on the surface of calcium carbonate particles. The solubility of hydroxyapatite decreases rapidly with an increase of pH and phosphate removal improves with increasing pH values. Essentially all orthophosphate is precipitated at values exceeding 9.5.

At values less than 9.5, phosphorus is adsorbed on the calcium carbonate formed. Since calcium carbonate is the only combined form from which lime is readily recovered, lime reuse may not be practical if the lime dose is not sufficient to drive the pH value above 9.5, thereby enhancing the creation of calcium carbonate.

Figure 4 shows the effect of lime dosages on final phosphorus concentration and pH for a typical wastewater. The lime dose required to achieve a given pH, settled water turbidity and/or phosphorus removal is primarily a function of the wastewater alkalinity and is relatively independent of the influent phosphorus concentration. However, in the case of phosphorus removal with iron or aluminum salts, increasing phosphorus concentrations require increasing concentrations of iron or aluminum ions (9).
b. Chemical Selection - Each of the chemicals described has assets and the final chemical selection for application of phosphate removal must be based on an economic analysis of various alternatives. This will ensure that a viable, least-cost system for a given set of operating conditions will be obtained. According to Evers (9) some of the important variables for any system include:

1. size of the facility;
2. degree of phosphorus removal required, including removal efficiency and final effluent concentration;
3. operational consistency required;
4. chemical characteristics of raw wastewater;
5. effect of adding sulfate or chloride (from alum or iron salts) on water quality;
6. operating methods and flexibility;
7. chemical costs to plant site; and
8. method of sludge handling and disposal.

c. Tertiary Treatment - Recently, tertiary treatment modules have been added to existing secondary facilities to upgrade the treatment efficiency beyond that previously attainable. Because coagulation/flocculation is a process of high operating and low capital costs, it is an attractive process alternative for upgrading new or existing wastewater treatment facilities, and as a process for removal of phosphorus compounds (16). The metal ions commonly used as coagulants -- Fe$^{3+}$, Al$^{3+}$ or Ca$^{2+}$ -- perform excellently to precipitate orthophosphates as well as the condensed polyphosphates. In a study conducted by McLellon and others (16), minimum residual phosphate levels have been recorded less than 0.1 mg/liter as PO$_4^{3-}$ following the addition of Fe$^{3+}$ as a coagulant. Using lime coagulation for the South Lake Tahoe wastewater, Wilson and Evans (8) report final clarifier effluent phosphorus concentrations range between 0.2 and 0.6 mg/liter as PO$_4$.

Normally these chemicals are added to raw sewage influent and phosphorus-containing precipitants are removed in the primary sedimentation units. Effluent from these units is then treated in conventional secondary biological processes. Alternatively chemicals have been added in the aeration tank or in the line leading to the activated sludge settling tanks where the phosphorus-precipitating floc is deposited with the organic floc. The chemical coagulation of secondary effluent at the South Lake Tahoe Plant typically removes 95 percent of the phosphorus compounds it receives (6).
The degree of clarification to be obtained by the addition of chemical coagulants is largely dependent upon the quantity of chemicals used and the care with which the process is controlled. It is possible to obtain by the coagulation/flocculation process a clear effluent, substantially free from suspended, colloidal material. From 80 to 90 percent of the total suspended matter, 50 to 55 percent of the total organic matter, and 80 to 90 percent of the bacteria can be removed by chemical precipitation. These figures can be compared with plain sedimentation in which 50 to 70 percent of the total suspended matter and 30 to 40 percent of the organic matter is removed (28).

Plants are achieving various levels of phosphate removal by adding either iron or aluminum salts to the primary clarifier, to the aeration basin and in separate chemical clarifiers following the secondary clarifier. In these applications, final effluent phosphorus concentrations of 1-3 mg/liter as P are generally obtained, depending on the type of chemical and application point. To achieve a final concentration less than 1 mg/liter as P, post-filtration must be employed (28).

d. Sludge Disposal - The most common methods of land disposal of chemical sludge include spreading on soil, lagooning, dumping and landfill. The disposal of digested sludge at sea is used by many large coastal cities. The chemical conditioning of sludge during the digestion process is attaining greater use because of the economy of increased solids yields and greater operational flexibility obtained.
Chemical addition results in the coagulation of the solids and the release of the adsorbed water. Chemicals used include ferric chloride, lime, alum and organic polymers. It is possible that current developments of effective pure-product recovery methods would permit recycling of the chemical precipitant, allowing a reduction in chemical costs and alleviating much of the disposal problem (28).
REFERENCES


